Title	On the Possibilities of the Attainment to Azeotropic Conditions in the Copolymerization of Vinylacetate and Acrylonitrile
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are inbeded to the shaft so as to form a screw line when radially connected from one to the next.

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33. On the Possibilities of the Attainment to Azeotropic Conditions in the Copolymerization of Vinylacetate and Acrylonitrile

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As already known in two-components systems, the azetoropic conditions are attained following cases;

$$\frac{r_1M_1+M_2}{M_1+r_2M_2}=1$$

at the equation of the composition;

$$\frac{dM_1}{dM_2}=\frac{M_1}{M_2}\cdot\frac{r_1M_1+M_2}{M_1+r_2M_2}$$

in which M_1 and M_2 represent the concentration of comonomers, r_1 and r_2 the monomer reactivity ratios respectively.

In this paper, we considered on the case of three-components and, finally found that the azeotropess in respect of M_1 and M_2 should be attained at the following conditions;

$$\frac{\left(r_1+\frac{M_2}{M_1}+C_1r_1\frac{M_3}{M_1}\right)\left(2+C_2r_2\frac{M_3}{M_1}\right)}{\left(C_1+r_2\frac{M_2}{M_1}+C_2r_2\frac{M_3}{M_1}\right)\left(2+C_1r_1\frac{M_3}{M_2}\right)}=$$

in which $r_1=k_{11}/k_{12}$, $C_1=k_{13}/k_{11}$ and $C_2=k_{23}/k_{22}$. Putting $M_3/M_1==x$ and $M_2/M_1=K$, then;

$$(r_1+K+C_1r_1x)(2+C_2r_2x)=(1+r_2K+C_2x)\left(2+C_1r_11\frac{K}{1}x\right)$$

From above equation, we will obtain x at giving C_1, C_2, r_1, and r_2, and also K.

At the copolymerisation of vinylacetate and acrylonitrile with using diethylfumarate or trichloroethylene as the third components, x was obtained as a larger value than unity. Therfore the azeotrope was found to be practically impossible to attain by these directions.

As the secondary direction for research on these possibilities, the effects of polym.-temperature on the changes of values of r are examined. The results are abulated as follows;

Polym. Temp.	r_1	r_2
25°C	2.5 ± 0.21	0.14 ± 0.02
65°C	7.0 ± 2	0

Then the conditions of $r_1>1$ and $r_2>1$, could not be attained at ordinary temperature range.

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34. Studies on Chemical Reactions of Polyvinyl Compounds

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Kinetics of deacetylation of polyvinyl acetate was discussed. The theory was in good agreement with experimental results, and based on this theory velocity constansts of elementary reactions were caculated. Assuming that acetyl groups which have hydroxyl groups as their neighbour can be more easily deacetylated than other, it was conclused that at the initial stage of the reaction apparent velocity constant must increase nearly proportionally to the reaction degree. This is in good accordance witn experimental results.

In connection with this reaction, saponification velocity of di-ester was also studied. In this case, apparent velocity constant can never be greater than twice of that at initial reaction.

Reaction velocity of acetalization and simultaneous acetalization-acetylation of polyvihyl alcohol was also discussed. The conclusion may be expressed as follows.

$$K_1 = K_0 \left\{1-\frac{2X^2}{(2-X)^3}\right\} \qquad (1)$$

$$K_2 = K_0 \left\{1-\frac{2(X+2Y)^2}{(2-X)^3}\right\} \qquad (2)$$

where K_1 and K_2 are apparent velocity constants, K_0 that of initial reaction, and X, Y ara degree of acetalization and acetylation in mole fraction. K_1 becomes O when X reaches a value of 0.8603. This value is in good accordance with 0.8647 obtained by P. J. Flory.

Mixed acetalization of polyvinyl alcohol was also studies, and it was suggested that exchange of acetal A and aldehyde B, and of acetal B and aldehyde A should be considered.